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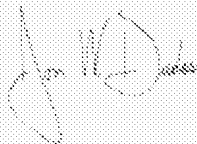
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## PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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INVENTOR(S)					
Given Name (first and middle [if any])		Family Name or Surname		Residence (City and either State or Foreign Country)	
YANG JUN LIPING		YANG HE MA		LOS ANGELES, CALIFORNIA LOS ANGELES, CALIFORNIA LOS ANGELES, CALIFORNIA	
<input type="checkbox"/> Additional inventors are being named on the _____ separately numbered sheets attached hereto					
TITLE OF THE INVENTION (500 characters max)					
THREE-TERMINAL ORGANIC MEMORY CELLS					
CORRESPONDENCE ADDRESS					
Direct all correspondence to:					
<input type="checkbox"/> Customer Number _____					
OR					
<input checked="" type="checkbox"/> Firm or Individual Name		David J. Oldenkamp, Esq. Shapiro & Dupont LLP			
Address		Suite 700			
Address		233 Wilshire Boulevard			
City		Santa Monica	State	California	ZIP 90401
Country		USA	Telephone	(310) 319-5411	Fax (310) 319-5401
ENCLOSED APPLICATION PARTS (check all that apply)					
<input checked="" type="checkbox"/>	Specification Number of Pages	11	<input type="checkbox"/>	CD(s), Number	
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<input checked="" type="checkbox"/> No.					
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____					

[Page 1 of 1]

Respectfully submitted

SIGNATURE

*David J. Oldenkamp*

TYPED or PRINTED NAME

DAVID J. OLDENKAMP

TELEPHONE

(310) 319-5411

Date

December 3, 2003

REGISTRATION NO.

29,421

(if appropriate)

Docket Number:

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# Three-Terminal Organic Memory Devices

Jun He, Liping Ma, and Yang Yang

Materials Science and Engineering  
University of California, Los Angeles, CA 90095

## Abstract

A novel high-performance organic electrical bistable device has been previously reported by our group, which has an Organic/Metal/Organic structure sandwiched between two aluminum electrodes.<sup>5,6</sup> We also have reported that the middle layer is incorporated with metal nanoclusters separated by thin oxide layers and proposed a model to explain the electrical bistability.<sup>8</sup> In this manuscript, we present results on the demonstration of a three-terminal organic memory device that has an organic/metal:organic/organic triple layer sandwiched between two electrodes. The two electrodes and the wired-out middle layer are the three terminals of the device. When the applied voltage on the device is larger than a critical voltage, the device switches from a high impedance state (off state) to a low impedance state (on state) and remains in the on state until a negative voltage is applied. When the device is biased between the two electrodes, the voltage is observed between the middle layer and the electrodes. We found that although the device is symmetric, the potential drop of the device is asymmetric; most of the voltage biased on the device drops on the bottom organic layer, especially when the device is in the off state, and the potential drop across the top organic layer increases dramatically when the device switches from the off state to the on state. Consequently, the state (on/off) can be known from the potential drop across the top organic layer when the device is biased. We propose that the decreasing in conductivity of the organic layers, especially the bottom organic layer, is the main reason for this

phenomenon. Results from the cyclic write-read-erase-read test and stress test of three-terminal organic memory device are also shown.

## **Introduction**

Devices with electrical bistability have been widely studied because they can be used as switches and memory elements, which are important for digital electrical instruments since they have two states of different conductivity. Reversible resistance switching process in inorganic thin film engendered strong interesting and much work has been done in this field. Recently, organic electrical switching and memory devices have attracted more attention<sup>1-11</sup> because of the distinct advantages of organic materials, such as light weight, mechanical flexibility, etc.

We previously have reported the invention of novel organic bistable devices (OBDs) and their electrical switching and memory effect.<sup>5-8</sup> Our devices consist of five thin films: organic/metal/organic triple layer sandwiched between two metal electrodes. When the voltage on the device is larger than a critical voltage, the device switches from a high impedance state (off state) to a low impedance state (on state) and remains in the on state until a negative voltage is applied. Recently, we used a metal and organic mixed layer by co-evaporation to replace the middle metal layer and found that the performance and yield of the devices improved. Although the devices work well, the mechanism of the OBDs is still not clear. In order to study the OBDs layer by layer, we wired out the middle layer to study the potential drop of the bottom and top organic layer when the OBD is biased. We found that although the device is symmetric, the potential drop of the device is asymmetric; most of the voltage biased on the device drops on the bottom

organic layer, especially when the device in the off state. Based on this phenomenon, three-terminal organic memory devices are created. A voltage is biased between the bottom and top electrode to operate the device, and at same time, the voltage between the top electrode and middle layer is observed to read the state (on/off) of the device. The change of the resistances of the top and bottom organic layer is discussed. Results from the cyclic write-read-erase-read test and stress test of the three-terminal organic memory device are also discussed.

## Experiments

The process of device fabrication is similar with what we previously reported.<sup>5,6</sup> The glass substrate is cleaned by a routine procedure. First, precleaned glass substrate is sonicated in the order of detergent, deionized water, acetone and isopropanol, and then baked in an oven at about 80°C to prepare for fabrication. Five layers of OBDs are deposited layer by layer by thermal evaporation at high vacuum (pressure of the evaporator is below  $2.0 \times 10^{-6}$  Torr) without breaking the vacuum. The organic compound and metal material we used are 2-amino-4,5- imidazoledicarbonitrile (AIDCN) and aluminum (Al) respectively. At first, a 650 Å Al film was deposited on the cleaned glass substrate at a deposition rate of 3 Å/s for the bottom electrode, 400 Å of AIDCN film was deposited (0.5 Å/s) on it as the bottom organic layer, then 200 Å of Al and AIDCN mixed film was deposited by co-evaporation. The deposition rate of Al and AIDCN for the middle layer are 0.4 Å/s and 0.1 Å/s. Then another 450 Å AIDCN film (deposition rate: 0.5 Å/s) and 800 Å Al film (deposition rate: 2 Å/s) were deposited sequentially to form top organic and electrode layers. The cross-sectional area of the top and bottom electrodes is  $0.4 \text{ mm}^2$ , which is the size of OBDs mentioned in this paper. In

order to study the mechanism of OBDs and investigate the potential distribution of the device, we wired out the middle metal layer during device fabrication. When the mixed middle layer was deposited on the bottom AIDCN layer, it was also deposited on extra bottom electrodes for wiring it out and a strip of the mixed film was deposited on the glass substrate at the same time for study the mixed film itself.

The thickness of thermally evaporated organic and metal thin films are monitored by a quartz crystal calibrated with Dektak IIA. Current-voltage curves reported here were measured with a HP 4155B semiconductor parameter analyzer. The curves of the cyclic write-read-erase-read test and stress test were characterized by two Keithley 2400 Series Sourcemeters (one for biasing the voltage, another one for measuring the potential drop) controlled by a computer. All electrical measurements were done in ambient condition. The schematic diagram of an OBD with a mixed middle layer and the chemical structure of AIDCN are shown in Fig. 1.

## **Results and discussion**

Previously, only the I-V characteristics of the whole device were studied. Typical I-V curves for OBDs are shown in Fig. 2. During the first forward bias scan from 0 to 3 volts, the device shows a very low current in the low-voltage range, indicating the device is in the off state. At a critical voltage (it is 1.5 volts here), the current has a sharp increase of several orders of magnitude, indicating the device has had a transition from the off state to the on state. However, the I-V curve recorded in the second bias scan is totally different from that observed in the first bias scan. Even in the low-voltage range, the device shows very high current, indicating that the device remains in the on state. When the device is switched to the on state, it remains in that state even when the power

is off. The off state can be recovered by applying a reverse bias, which means this kind of device is ideal for memory applications.

When we measured the I -V curves of OBDs, a sweeping voltage was biased between the top Al electrode and bottom Al electrode, and the change in potential of the middle mixed layer is observed at same time. The I-V curves and the changing potential drop on AIDCN layers during the switch-on process of a device are shown in Fig. 3, where triangles represent the I-V curve of the device and circles and squares represent the potential drop of top and bottom AIDCN layer respectively.

In Fig. 3a, the common electrode for biasing and measurement is the top Al electrode, so the potential measured is the voltage drop across the top AIDCN layer (defined as  $U_{top}$ ).  $U_{top}$  increases from 2 mV to 400 mV when the device transitions from the off state to the on state at around 0.9 volts. The potential drop of bottom organic layer (defined as  $U_{bot}$ ) can be obtained by subtracting  $U_{top}$  from the biased voltage.  $U_{bot}$  changes very smoothly while sweeping the voltage, but decreases slightly more when the device switches from the off state to the on state. When the device is in the off state, almost all the voltage on the device drops on the bottom AIDCN layer, and in the on state, the values of  $U_{top}$  and  $U_{bot}$  are of the same order and comparable.

In Fig. 3b, the polarity of the scan voltage changed - the common electrode is the bottom Al electrode during the measurement, so  $U_{bot}$  is measured and  $U_{top}$  is calculated. The device switch-on occurs at the same voltage with Fig. 3a. In order to compare with the curves in Fig. 3a, the bias voltage is scanned from 0 to -2 volts such that the directions of electrical field are the same in Fig. 3a and Fig. 3b. Fig. 3b is almost the



same as Fig. 3a except for small differences, that  $U_{\text{bot}}$  has no distinct change while  $U_{\text{top}}$  increases two orders at the transition voltage of the device.

The I-V curve of the middle mixed film strip on a glass substrate is shown in Fig. 4, where the size of the thin film is 10mm by 3 mm. The strip is deposited on glass when the mixed middle layer is deposited on the bottom AIDCN film, so the thickness of the strip is also 200 Å. The I-V curve in Fig. 4 is a perfect straight line, which means the middle mixed layer shows ohmic behavior, and the resistance of the strip is about 79 KΩ. From this, we can see that the conductivity of the mixed middle layer is quite large, the potential measured by wiring out the middle layer is reliable, and the potential drop on the mixed middle layer can be ignored.

Fig. 5 shows the current through the OBD,  $U_{\text{top}}$  and the resistance of the top and bottom AIDCN layer during switch-on process and on state. In Fig. 5a, during the first sweep (squares), the current through the OBD and the potential drop of the top AIDCN layer increase three orders at the same time sharply when the sweeping voltage increases to 2 volts, and the OBD is switched on. During the second sweep (circles), the OBD remains in the on state, and the current and  $U_{\text{top}}$  are much higher compared to the off state. It is clear that the changes in current and  $U_{\text{top}}$  are synchronous in the off and on state. We can get the resistance of the top and bottom AIDCN layer from dividing  $U_{\text{top}}$  and  $U_{\text{bot}}$  by the current. The resistance-voltage curves of the top and bottom AIDCN layer calculated from the data of Fig. 5a are shown in Fig. 5b, where the open curves show the resistance change of the top AIDCN layer and solid curves show the change of the bottom AIDCN layer. From Fig. 5b, we can see that when the OBD is in the off state, the resistance of the bottom AIDCN (defined as  $R_{\text{bot}}$ ) is about 5 orders larger than the resistance of the top

AIDCN layer (defined as  $R_{top}$ ). This is the reason why  $U_{top}$  is very small and most of the voltage is dropped at the bottom AIDCN layer in the off state. When the OBD switches from off to on, both  $R_{bot}$  and  $R_{top}$  decrease sharply, but  $R_{bot}$  decreases about 4 orders while  $R_{top}$  only decreases 1 order. At the on state,  $R_{bot}$  is about 50 times  $R_{top}$ , so  $U_{top}$  increases sharply during the transition of OBD from the off state to the on state. When the OBD remains in the on state,  $R_{bot}$  and  $R_{top}$  have no obvious change while sweeping the voltage. From Fig. 5, we know that the decreasing of  $R_{bot}$  plays a more important role for the switching of the OBD, and the bottom organic layer of the OBD should be studied more thoroughly in order to understand the mechanism of the OBD.

Although the thickness of the bottom and top AIDCN layers are almost identical,  $R_{bot}$  is much bigger than  $R_{top}$  at on state and off state. The probable reason is that the interfaces of the two AIDCN layers are different. When the mixed middle layer was deposited on the bottom AIDCN layer, a few Al atoms penetrated the bottom AIDCN layer because of the low deposition rate and the co-deposition with AIDCN, and the interface between the bottom AIDCN and mixed middle layer is not clear. When the top electrode was deposited, lot of Al atoms penetrated in the top AIDCN layer due to the high deposition rate. The morphology of the bottom Al is flatter than the mixed middle layer, which is another reason for the uneven potential distribution. The mixed middle layer plays an important role in the OBD, and we believe the middle mixed layer is nano-structured. The reason for huge decrease of  $R_{bot}$  when the device is switched on is probably due to space charges accumulating at the nano-particles in the mixed middle layer. This results in some charges induced in the AIDCN layer near the middle and the conductivity of AIDCN increases.

Based on these results and discussion, a new type of OBD with three terminals was created. Top electrode, bottom electrode and mixed middle layer are the three terminals of the OBD, which act as ground, control and read terminal respectively. Top electrode is just the common electrode for biasing and measuring the voltage; the bottom electrode is used to control the state of the OBD (bias a voltage to switch on/of the device) and bias the small voltage read the state (on/off) of the device, just as shown in Fig. 1a. The readout of the three-terminal OBD is different than the previous two-terminal OBD. A low level voltage (100 mV magnitude at on state and below 1 mV at off state) is needed to measure in order to read the state of the device, while a low level current (1  $\mu$ A at on state and below 10nA at off state) is needed for the two-terminal OBD. Because a 100mV voltage is easier to measure than a 1  $\mu$ A current and the fabrication technology for these two kinds of OBD is the same, the three-terminal OBD is more practical.

In order to study the stability of the device at on and off state, a constant small voltage is biased on the device and  $U_{top}$  is recorded to monitor the state of the OBD when the OBD stays in the on or off state. Fig. 6 shows the stress test of the on state and off state of a three-terminal OBD biased at 1 volt. The inset of Fig. 6 shows the switch-on process and on state of the device. The switch-on voltage for this three-terminal OBD is 2.0 volts. In Fig. 6,  $U_{top}$  at on state is 3 orders bigger than the off state, and it can be seen that there is no significant degradation of the device in either the on or off state during the three-hour stress test, indicative that both states are stable.

In Fig. 7, we present the rewritable data-storage application of three terminal OBD. The device was biased by a multi-step voltage to switch on (write), read, switch off (erase) and read it. The voltage for write, erase and read is 2.5 volts, -1.5 volts and 1 volt

respectively. The ratio of  $U_{top}$  in the on and off state is about  $10^3$  during the test. At the beginning, the success ratio of the cycle (write-read-erase-read) is almost 100 %. After 21 hours of continual testing, the device still worked very well, and the ratio was still near 100%, but  $U_{top}$  at the off state increased 1.5 orders from 0.1 mV to 10 mV indicating the device degraded during the test since the test was operated in air. It should be noted that the time scale used in Fig. 7 is due to the inherent limitation of the test instrument and program.

## Conclusions

In conclusion, we have demonstrated that the potential distribution in the organic bistable device with the organic/metal:organic/organic triple layer structure sandwiched between two metal electrodes is asymmetric. When the device switches from the off state to the on state, the potential drop on the top organic layer has a sharp jump while the potential drop on the bottom organic layer has small change. The reason is that the resistance of the bottom organic layer decreases several orders when the device is switched on. A novel three-terminal organic bistable device is proposed. The stress test and cyclic read-write-erase test of the device shows that the device has pretty good stability at the off and on states, and also have a stable rewritable feature. The detailed operating mechanism is under further study.

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## Figure captions

Figure 1. A diagram of OBD with a co-evaporated middle layer and the measurement setup (a), and the chemical structure of AIDCN (b).  $V_{\text{bias}}$  means the voltage biased on the OBD,  $V_{\text{meas}}$  means the voltage measured.

Figure 2. I–V characteristics of an OBD recorded during the switching on process and the on state.

Figure 3. The I–V curves and the change of the potential drop on AIDCN layers during the switching-on process of the OBD. The common electrode is the top Al electrode in figure 3(a) while the common electrode is the bottom Al electrode in figure 3(b).

Figure 4. I–V characteristics of the mixed middle thin film on a glass substrate with a size of 10 mm by 3 mm and thickness of 200 Å.

Figure 5. (a) I–V curve of the OBD, and potential drop of the top AIDCN layer during sweeping from 0 to 3 volts during the switch-on process and in the on state; (b) The change of the resistance of top and bottom AIDCN layer during the switch-on process and in the on state.

Figure 6. Stress test of the on and off states of a three-terminal OBD biased at 1 volt. Inset shows the potential drop across the top AIDCN layer during the switch-on process and in the on state of the device.

Figure 7. Cyclic write-read-erase-read test of the three-terminal OBD. The upper curve is the voltage biased on the device and the bottom curve is the potential drop across the top AIDCN layer of the device. The voltage for write, erase and read is 2.5 volts, -1.5 volts and 1 volt. In order to use a logarithmic axis for the potential drop across the top AIDCN layer, the current of erasing process is an absolute value. Fig. 7a is the beginning of the cyclic test while Fig. 7b is that recorded after 21 hours of continual testing.

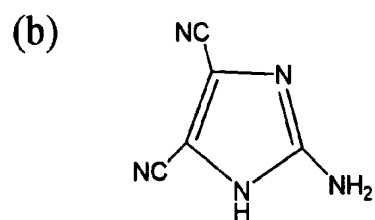
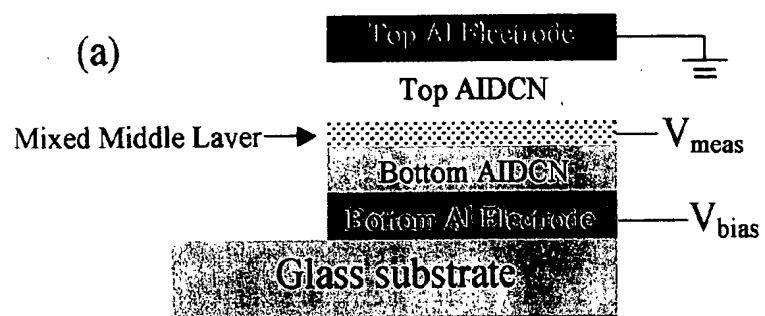


FIG. 1

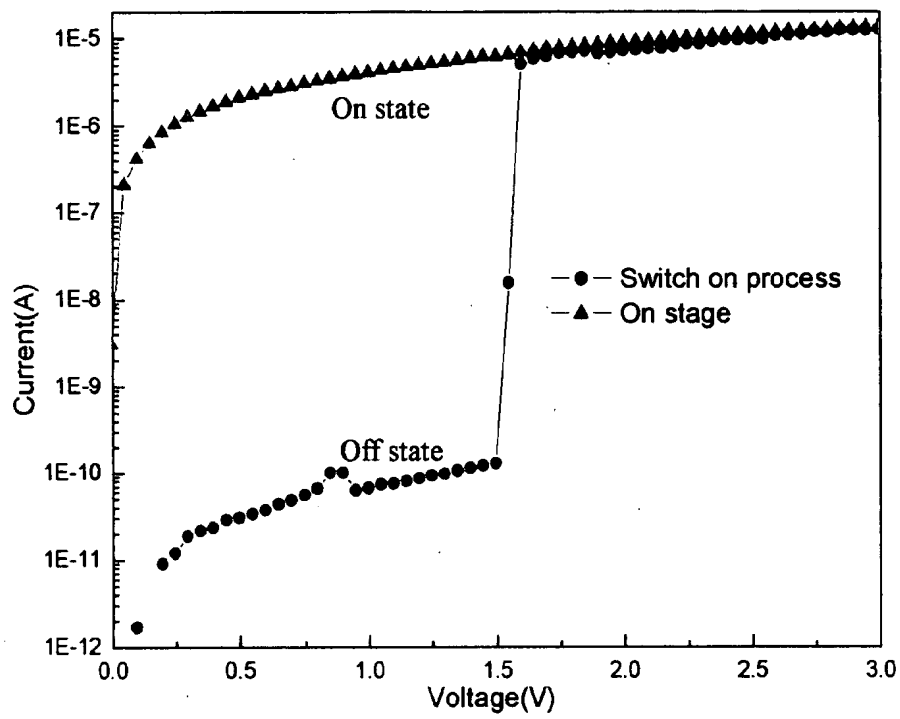


FIG. 2



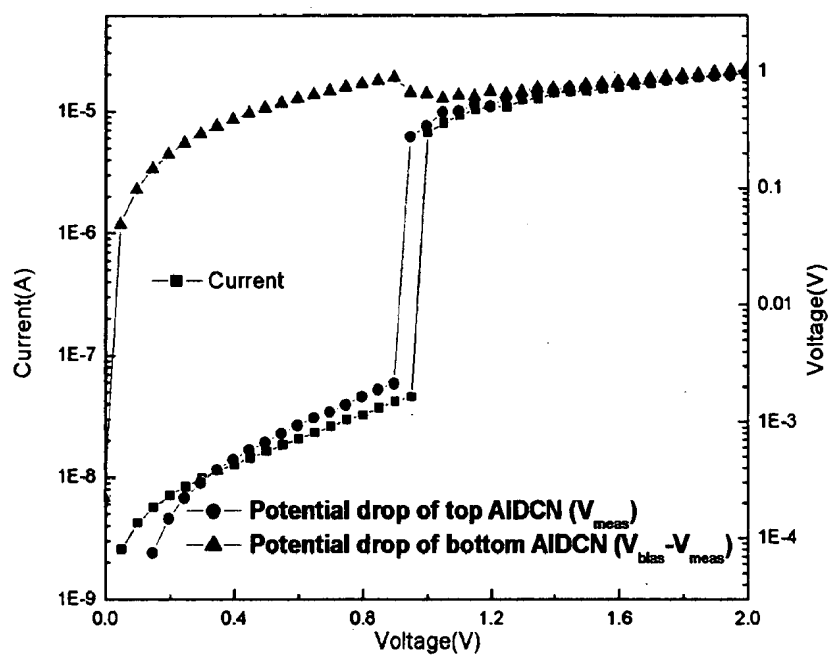


FIG. 3a

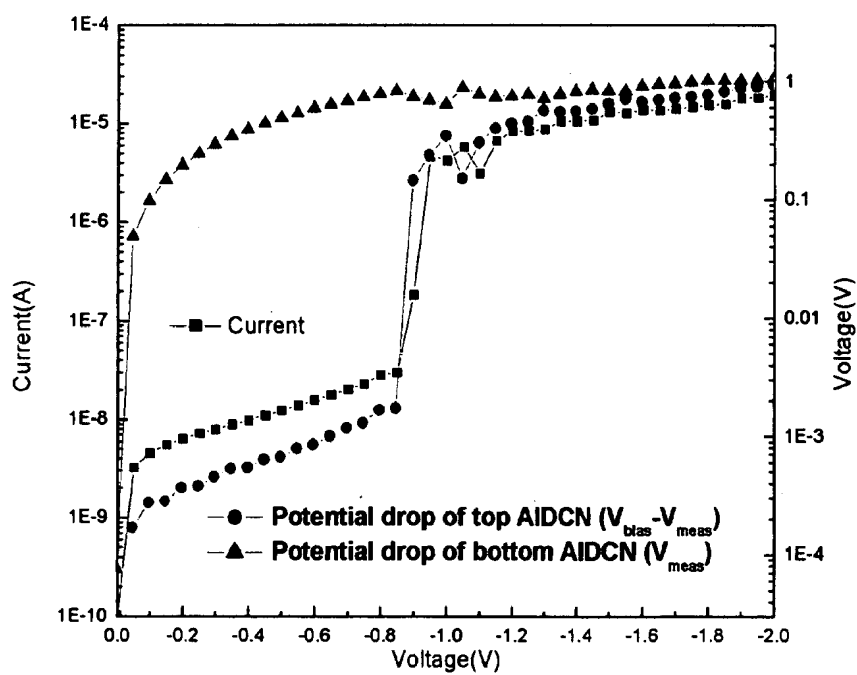


FIG. 3b

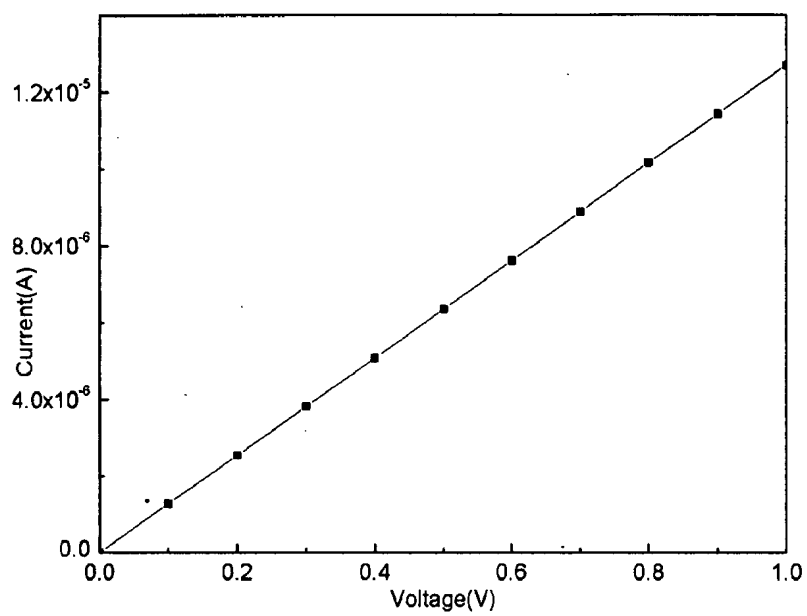


FIG. 4

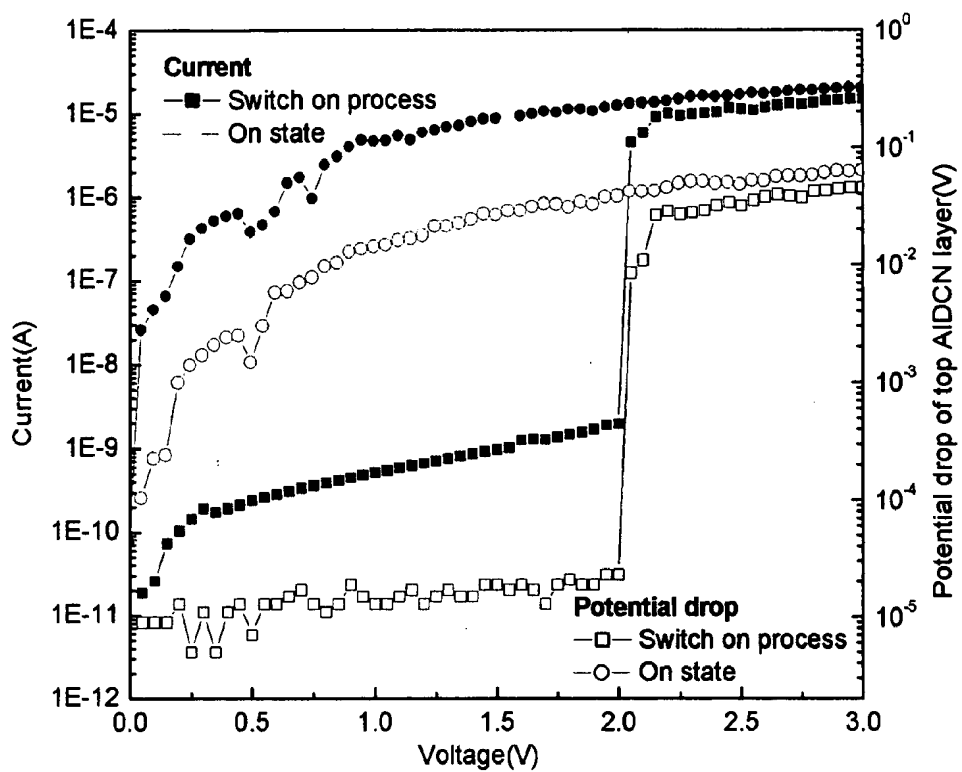


FIG. 5a

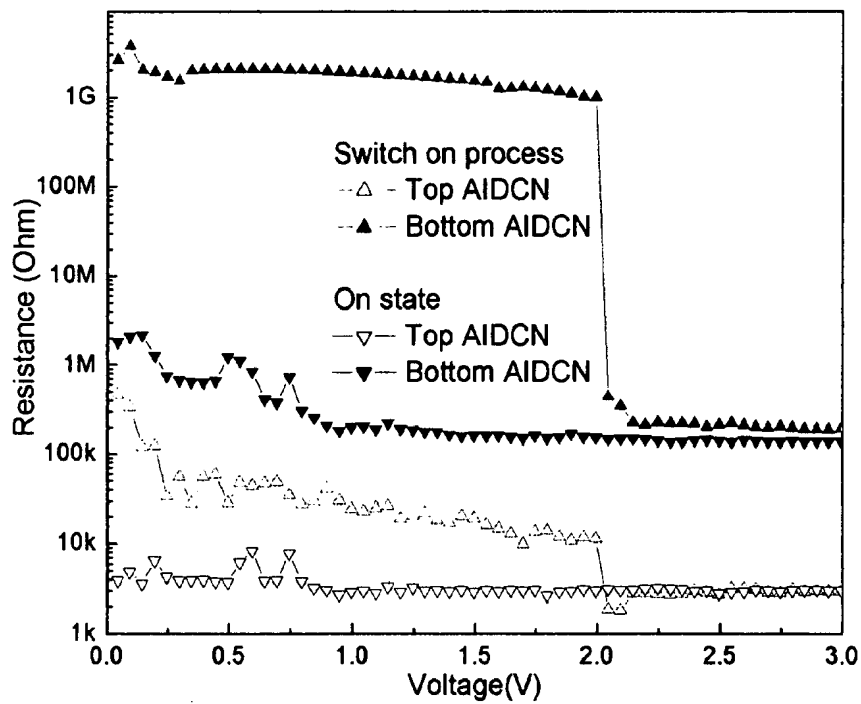


FIG. 5b

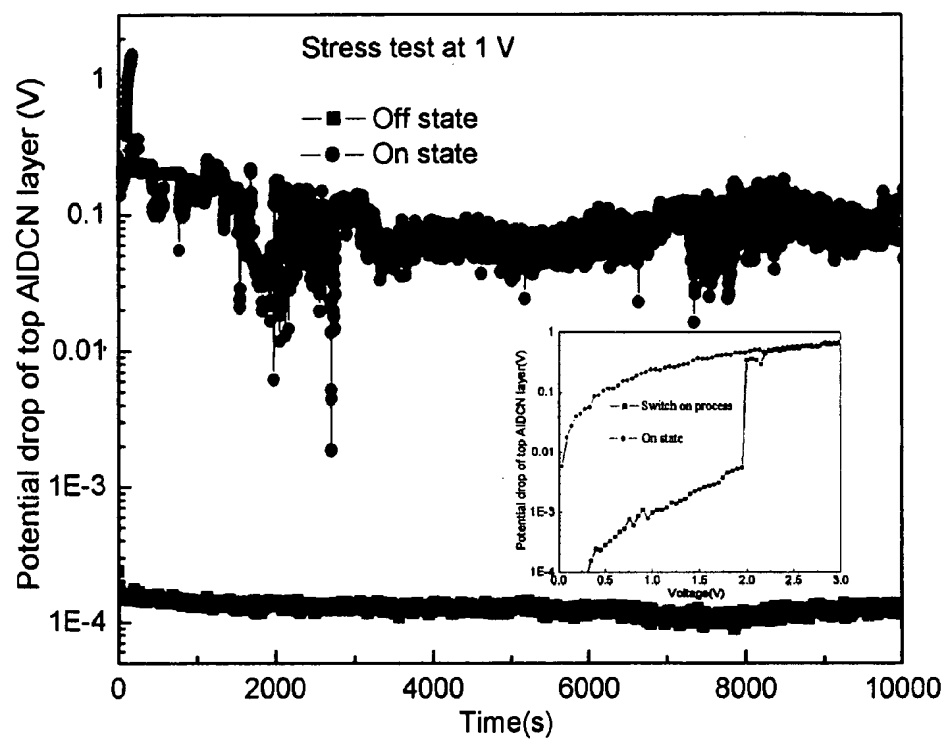


FIG. 6

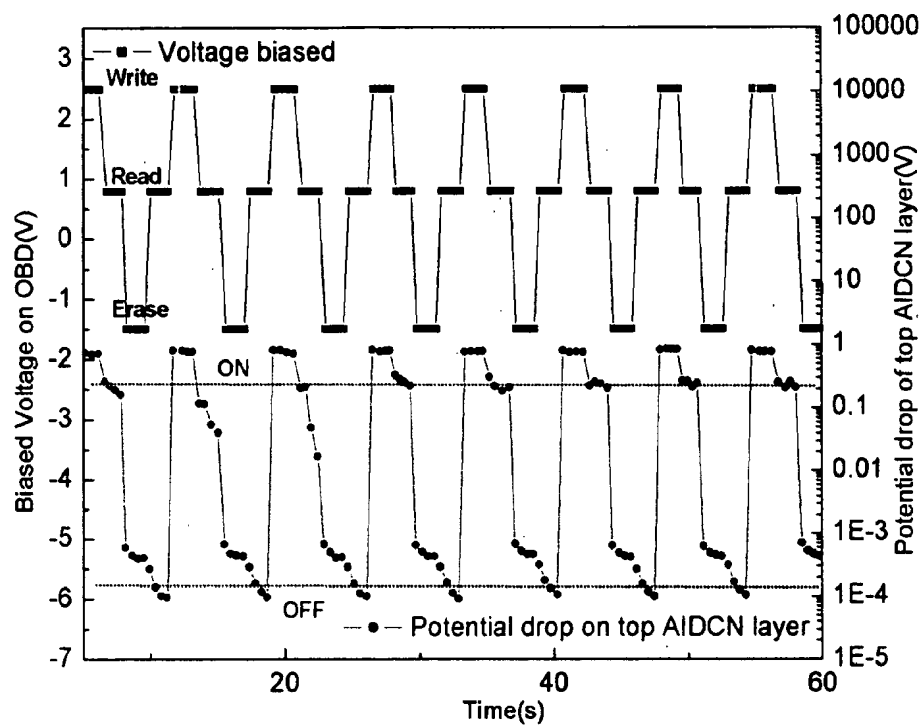


FIG. 7a

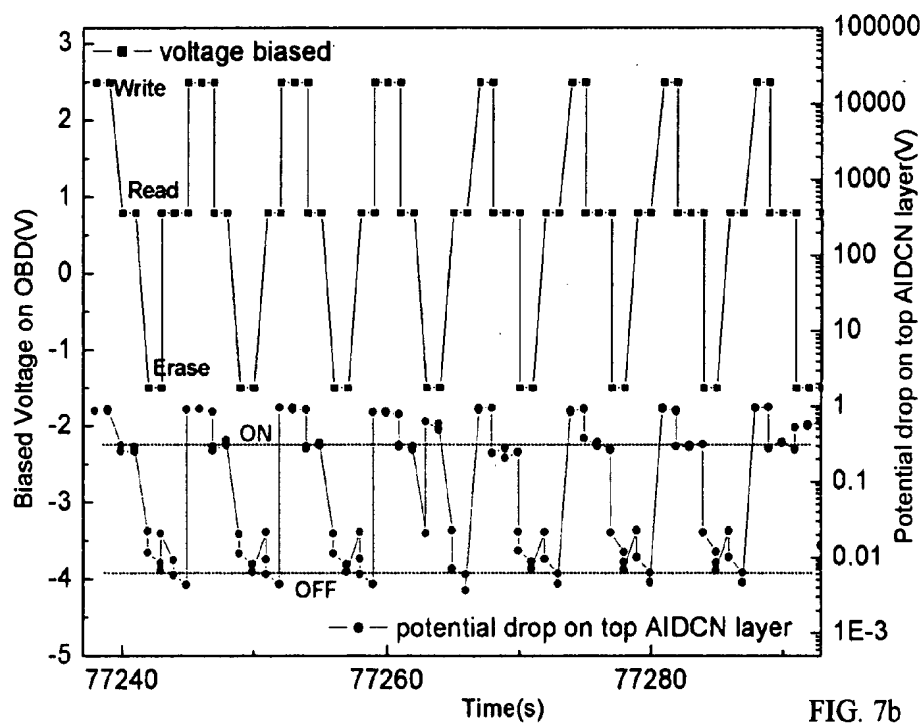


FIG. 7b

## Initial Information Data Sheet

### INVENTOR INFORMATION

Inventor One Given Name::	Yang
Family Name::	Yang
Postal Address Line One::	6531 Boelter Hall
City::	Los Angeles
State or Province::	California
Postal or Zip Code::	90095
City of Residence::	Los Angeles
State or Prov. of Residence::	California
Country of Residence::	US
Citizenship Country::	US
Inventor Two Given Name::	Jun
Family Name::	He
Postal Address Line One::	6531 Boelter Hall
City::	Los Angeles
State or Province::	California
Postal or Zip Code::	90095
City of Residence::	Los Angeles
State or Prov. of Residence::	California
Country of Residence::	US
Citizenship Country::	Peoples Republic of China
Inventor Three Given Name::	Liping
Family Name::	Ma
Postal Address Line One::	6531 Boelter Hall
City::	Los Angeles
State or Province::	California
Postal or Zip Code::	90095
City of Residence::	Los Angeles
State or Prov. of Residence::	California
Country of Residence::	US
Citizenship Country::	Peoples Republic of China

### CORRESPONDENCE INFORMATION

Name Line One::	David J. Oldenkamp, Esq.
Address Line One::	Shapiro & Dupont LLP
Address Line Two::	233 Wilshire Boulevard
Address Line Two::	Suite 700
City::	Santa Monica
State or Province::	CA
Postal or Zip Code::	90401
Telephone::	(310) 319-5411
Fax::	(310) 319-5401

**APPLICATION INFORMATION**

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